

PART ONE
TRIARYLPYRIDYLMETHANES

PART TWO
RESTRICTED ROTATION IN SUBSTITUTED
DIAMINOMESITYLENES

PART THREE
HINDERED TETRAARYLMETHANES

BY

JOHN B. CAMPBELL

B.S., University of Kansas, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

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ACKNOWLEDGMENT

The author wishes to express his appreciation to Professor Roger Adams for advice and guidance during the course of these investigations.

He is indebted to the Allied Dye and Chemical Company for the fellowship held since September, 1948.



PART ONE

TRIARYLPYRIDYLMETHANES

INTRODUCTION

It has been found that the condensation of triphenylchloromethane with 2-hydroxypyridine yields 5-triphenylmethyl-2-hydroxypyridine (1). In the present work, a study was made to determine the scope of the reaction and the possible conversion of the hydroxypyridines to the corresponding pyridines.

DISCUSSION OF RESULTS

The condensation of triphenylcarbinol with 2-hydroxypyridine employing a trace of sulfuric acid catalyst proceeded slightly better than the condensation using triphenylchloromethane. Similar results were obtained upon condensation with 3-methyl-2-hydroxypyridine. In an analogous manner, the condensations of diphenylxenylchloromethane or diphenylxenylcarbinol plus a trace of sulfuric acid catalyst with 2-hydroxypyridine and with 3-methyl-2-hydroxypyridine were carried out. In all cases the yields amounted to 45-55%.

The condensation of triphenylcarbinol with 6-methyl-2-hydroxypyridine gave a low yield of product, assumed to be 3-triphenylmethyl-6-methyl-2-hydroxypyridine. The hydroxyl grouping in the product was very inert, presumably due to the steric hindrance of the neighboring triphenylmethyl group.

The 5-triarylmethyl-2-hydroxypyridines were converted in nearly quantitative yields to the corresponding 5-triarylmethyl-2-chloropyridines by means of phosphorus oxychloride. It was found necessary to carry out the reactions in a closed system.

Catalytic reduction of the 5-triarylmethyl-2-chloropyridines afforded the corresponding triarylpseudomethanes in excellent yield.

Triphenyl- β -pyridylmethane was found to be very similar to tetraphenylmethane with respect to physical properties, infrared spectrum and phosphorescence after irradiation with ultraviolet light.

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PART TWO

RESTRICTED ROTATION IN SUBSTITUTED DIAMINOMESITYLENES

INTRODUCTION

cis and *trans* Isomers due to restricted rotation about the carbon-nitrogen bond were obtained in the synthesis of a variety of N,N'-dialkyl-N,N'-diarylsulfonyldiaminomesitylenes (1,2). In the present work there were studied a number of compounds in which the nitrogen atoms of the diaminomesitylene molecule are incorporated in five-membered ring systems.

DISCUSSION OF RESULTS

As a model experiment, diaminomesitylene was disuccinylated with succinic anhydride. Ring closure of the N,N'-disuccinyldiaminomesitylene gave disuccinimidomesitylene. In a similar manner, bis-(α,α -dimethylsuccinimido)-mesitylene and bis-(3-nitrophthalimido)-mesitylene were obtained in over 90% yield by ring closure of the corresponding diamido diacids. No *cis-trans* isomers were obtained.

The reaction of methyl β -chlorosulfonylpropionate with diaminomesitylene afforded N,N'-di-(β -carbomethoxyethane-sulfonyl)-diaminomesitylene. Hydrolysis of the ester group-

ings in the latter and ring closure of the resulting dicarboxylic acid gave a 75% yield of bis-(propionyl-sulfinido)-mesitylene. No isomers were isolated

The reaction of γ -bromopropanesulfonyl chloride, prepared by way of trimethylene bromide and γ -bromopropyl thiocyanate, with diaminomesitylene gave a low yield of N,N'-di-(γ -bromopropanesulfonyl)-diaminomesitylene. Ring closure of the latter gave a nearly quantitative yield of bis-(N-trimethylenesulfonamido)-mesitylene. Again no isomers resulted. An analogous compound, N,N'-dimethyl-N,N'-dimethanesulfonyldiaminomesitylene, which has the five-membered rings opened, was prepared by the methylation of N,N'-dimethanesulfonyldiaminomesitylene. It was readily obtained as a mixture of *cis* and *trans* isomers. Infrared spectra of nitromethane solutions of the isomers showed they were not isomorphous.

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PART THREE

HINDERED TETRAARYLMETHANES

INTRODUCTION

Optical isomerism due to restricted rotation in certain biphenyls (1) and aryl olefins (2) has been widely studied. However, no isomers have been obtained due to restricted rotation about a carbon-carbon bond in which one of the carbon atoms is fully saturated (3). In the present work, an attempt was made to obtain optical isomerism due to restricted rotation about the central saturated carbon atom of tetraarylmethanes containing the fluorene nucleus.

DISCUSSION OF RESULTS

The condensation of 9-hydroxy-9-o-tolylfluorene (I) with phenol, aniline, o-toluidine and p-xylydine gave good yields of the corresponding 4-(biphenylene-o-tolylmethyl)-substituted compounds. Attempted condensations with o-cresol, resorcinol and 2,5-dimethoxyaniline failed to yield crystalline products.

The attempted resolution of 4-(biphenylene-o-tolylmethyl)-2-methylaniline (II) by means of the crystalline salt from *d*-camphorsulfonic acid failed. No crystalline salts could be obtained from optically active acids and 4-(biphenylene-o-tolylmethyl)-2,5-dimethylaniline (III). The reaction of III with *d*-camphoric anhydride gave only one pure camphoramic acid in poor yield. A crystalline salt was readily obtained from quinine and the phthalamido acid obtained from III, but no resolution could be effected.

The attempted condensation of I with 8-amino-2,4,7-trimethylquinoline (IV) failed. IV was prepared by the nitration of 2,4,7-trimethylquinoline (V) and subsequent reduction of the nitro group. The synthesis of V was accomplished by ring closure of the anil resulting from *m*-toluidine and acetylacetone. That the ring closure had not yielded the isomeric 2,4,5-trimethylquinoline (VI) was shown by an unambiguous synthesis of the latter. Ring closure of the anil obtained from 3-amino-4-chlorotoluene and acetylacetone gave 8-chloro-2,4,5-trimethylquinoline, which yielded VI upon catalytic removal of the chlorine atom.

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VITA

The author was born December 8, 1925 at Licking, Missouri. He attended elementary school in St. Louis, Missouri, and graduated from Mexico High School, Mexico, Missouri, in June, 1942. From June, 1942, to June, 1943, he attended Central College, Fayette, Missouri. In August, 1943, he entered the University of Kansas. After serving in the United States Army from February, 1944, to May, 1946, he returned to the University of Kansas in June, 1946, receiving the degree of Bachelor of Science in June, 1947. He entered the Graduate College of the University of Illinois in June, 1947. An Allied Dye and Chemical Company Fellowship was held from September, 1948, to June, 1949.



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